Richard M. McCurdy Appln. No. 09/662,181

Amendment Under 37 CFR 1.116

## **LISTING OF CLAIMS**

This listing of claims will replace all prior versions and listings of claims in the application:

## LISTING OF CLAIMS:

Claims 1-32 (canceled).

33. (previously presented): A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath, positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature is from about 590° to 715°C (1100° to 1320°F);

directing titanium tetrachloride in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon.

- 34. (previously presented): The method of claim 33 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.
  - 35. (previously presented): A method comprising the steps of:

2

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

depositing a coating over at least one of the major surfaces by positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature range is from about 590° to 715°C (1100° to 1320°F), directing a precursor gas mixture comprising titanium tetrachloride and an organic oxygen containing compound, wherein the concentration of the titanium tetrachloride is in the range from about 0.1-5.0 % by volume, through said chemical vapor deposition coating apparatus over a surface of the float ribbon and annealing the float ribbon in air to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon.

- 36. (previously presented): The method of claim 35 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.
- 37. (previously presented): In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon;

moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing by chemical vapor deposition a crystalline phase of a photocatalyticallyactivated self-cleaning titanium dioxide coating over a surface of said float ribbon as the float ribbon is formed.

- 38. (previously presented): The method of claim 37 the improvement further comprising: depositing a silica coating over a surface of said float ribbon and depositing said titanium dioxide coating over said silica coating.
- 39. (previously presented): The method of claim 38 wherein said titanium dioxide coating has a thickness of 1300Å.
- 40. (previously presented): The method of claim 37, the improvement further comprising: depositing a silica layer over a surface of said float ribbon and depositing said photocatalytically-activated self-cleaning coating over said silica layer wherein the thickness of the silica layer is about 339Å.
- 41. (previously presented): A method comprising steps of:

  providing a glass article having at least one surface by a float manufacturing process;

  depositing a photocatalytically-activated self-cleaning coating over the surface of the

  article by chemical vapor deposition during the glass manufacturing process so that the coating

  has titanium dioxide in the crystalline phase and has a thickness of 1300Å.
  - 42. (previously presented): A method comprising the steps of: providing an article of manufacture having at least one surface;

depositing a silica layer by chemical vapor deposition having a thickness of about 339Å over said surface; and

depositing a photocatalytically-activated self-cleaning coating in a thickness of 490Å by chemical vapor deposition over said silica layer whereupon said silica layer inhibits migration of sodium ions from the surface of said article to said photocatalytically-activated self-cleaning coating, wherein the photocatalytically-activated self-cleaning coating is deposited from a precursor gas mixture comprising, by volume percent, 0.7% titanium tetrachloride, 17.2% ethyl acetate, 7.2% oxygen and 74.9% helium, with flow rates of 0.2 liters per minute titanium tetrachloride, 4.8 liters per minute ethyl acetate, 2.0 liters per minute oxygen and 20.9 liters per minute helium, the precursor gas mixture having a temperature above 300°F and below the decomposition temperature of ethyl acetate, the article of manufacture moving at a line speed of 300 inches per minute, and the article having a substrate temperature of 1170°F.

- 43. (canceled).
- 44. (previously presented): The method of claim 42 wherein the article is selected from the group consisting of: glass sheet and continuous glass float ribbon.
  - 45-46. (canceled).
  - 47. (previously presented): A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath, positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in

the manufacture of the float ribbon where the temperature range is from about 590° to 715°C (1100° to 1320°F);

directing titanium tetrachloride in a carrier gas stream through said chemical vapor deposition apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon whereby said coating has a photocatalytically activated self-cleaning reaction rate of  $8.1 \times 10^{-3}$  to  $9.1 \times 10^{-3}$  cm<sup>-1</sup> min<sup>-1</sup>.

- 48. (previously presented): The method of claim 47 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.
  - 49. (previously presented): A method comprising the steps of:

manufacturing a continuous glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

depositing a coating over at least one of the major surfaces by positioning a chemical vapor deposition coating apparatus over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature range is from about 590° to 715°C (1100° to 1320°F), directing a precursor gas mixture comprising titanium tetrachloride and an organic oxygen containing compound, wherein the concentration of the titanium tetrachloride is in the range from about 0.1-5.0% by volume, through said chemical vapor deposition coating apparatus over a surface of the float ribbon and annealing the float ribbon to produce titanium dioxide in

the crystalline phase as a photocatalytically-activated self-cleaning coating over the glass float ribbon whereby said coating has a photocatalytically activated self-cleaning reaction rate of  $8.1 \times 10^{-3}$  to  $9.1 \times 10^{-3}$  cm<sup>-1</sup> min<sup>-1</sup>.

- 50. (previously presented): The method of claim 49 wherein the directing of the metal oxide precursor is directly onto the surface of the float ribbon without any intervening coating layers.
- 51. (previously presented): In a method for forming a glass float ribbon wherein the method includes the steps of melting glass batch materials in a furnace; delivering the molten glass onto a bath of molten tin; pulling the molten glass across the tin bath whereupon the glass is sized and controllably cooled to form a glass float ribbon; removing the float ribbon from the tin bath; moving the float ribbon by conveying roller through a lehr to anneal the float ribbon; moving the float ribbon to a cutting station on conveying rollers where the ribbon is cut into glass sheets, the improvement comprising:

depositing by chemical vapor deposition a crystalline phase of a photocatalytically-activated self-cleaning titanium dioxide coating over a surface of said float ribbon as the float ribbon is formed whereby said coating has a photocatalytically-activated self-cleaning reaction rate of  $8.1 \times 10^{-3}$  to  $9.1 \times 10^{-3}$  cm<sup>-1</sup> min<sup>-1</sup>.

52. (previously presented): The method of claim 51 the improvement further comprising: depositing a silica coating over a surface of said float ribbon and depositing said titanium dioxide coating over said silica coating.

7

- 53. (previously presented): The method of claim 52 wherein said titanium dioxide coating has a thickness of 1300Å.
- 54. (previously presented): The method of claim 51, the improvement further comprising: depositing a silica layer over a surface of said float ribbon and depositing said photocatalytically-activated self-cleaning coating over said silica layer wherein the thickness of the silica layer is about 339Å.
- 55. (previously presented): A method comprising steps of:

  providing a glass article having at least one surface by a float manufacturing process;

  depositing a photocatalytically-activated self-cleaning coating over the surface of the

  article by chemical vapor deposition during the glass manufacturing process so that the coating

  has titanium dioxide in the crystalline phase and has a thickness of 1300Å whereby said coating

  has a photocatalytically-activated self-cleaning reaction rate of 8.1x10<sup>-3</sup> to 9.1x10<sup>-3</sup> cm<sup>-1</sup> min<sup>-1</sup>.

  Claims 56-86. (canceled).
- 87. (withdrawn): A titanium dioxide photocatalyst structure comprising: a transparent glass substrate having first and second opposing surfaces, said transparent glass substrate containing alkaline ingredients therein, the first surface of said substrate receiving light from an external light source;

a titanium dioxide film having first and second opposing surfaces, a light transmittance of said titanium dioxide film being at least 50% for light having a wavelength of 550 nm, the first surface of said titanium dioxide film being formed on the second surface of said substrate, whereby light transmitted from said external source through the first and second opposing

surfaces of said substrate and through the first surface of said titanium dioxide film to the second surface thereof causes photocatalytic activity to be generated on the second surface of said titanium dioxide film; and

a transparent precoat film interposed between the second surface of said substrate and the first surface of said titanium dioxide film.

- 88. (withdrawn): The titanium dioxide photocatalyst structure according to claim 87, wherein said transparent precoat film has a thickness of 0.02  $\mu$ m to 0.2  $\mu$ m.
- 89. (withdrawn): The titanium dioxide photocatalyst structure according to claim 88, wherein said precoat film is composed of SiO<sub>2</sub>.
  - 90. (withdrawn): A titanium dioxide photocatalyst structure comprising: a transparent substrate;

a titanium dioxide film formed on said substrate, said titanium dioxide film having photocatalytic activity and a light transmittance of at least 50% for light having a wavelength of 550 nm; and

a transparent precoat film disposed between the transparent substrate and the titanium dioxide film.

- 91. (withdrawn): The titanium dioxide photocatalyst structure according to claim 90 wherein the precoat film has a thickness of 0.02  $\mu$ m to 0.2  $\mu$ m.
- 92. (withdrawn): The titanium dioxide photocatalyst structure according to claim 90 wherein the precoat film is composed of SiO<sub>2</sub>.

- 93. (withdrawn): A method for producing a titanium dioxide photocatalyst structure according to claim 90 comprising a producing process which includes the step of forming the titanium dioxide film on the transparent substrate by a method selected from the group consisting of a pyro-sol method, a dipping method, a printing method and a CVD method.
  - 94. (withdrawn): A titanium dioxide photocatalyst structure comprising: a transparent substrate;

a titanium dioxide film formed on said substrate, said titanium dioxide film having a thickness of 0.1  $\mu$ m to 5  $\mu$ m, photocatalytic activity and a light transmittance of at least 50% for light having a wavelength of 550 nm; and

a transparent precoat film disposed between the transparent substrate and the titanium dioxide film.

- 95. (withdrawn): The titanium dioxide photocatalyst structure according to claim 94 wherein the precoat film has a thickness of 0.02  $\mu$ m to 0.2  $\mu$ m.
- 96. (withdrawn): The titanium dioxide photocatalyst structure according to claim 94 wherein the precoat film is composed of SiO<sub>2</sub>.
  - 97. (withdrawn): A titanium dioxide photocatalyst structure comprising: a transparent substrate;

a titanium dioxide film, containing an anatase crystal, formed on said substrate, said titanium dioxide film having photocatalytic activity and a light transmittance of at least 50% for light having a wavelength of 550 nm; and

a transparent precoat film disposed between the transparent substrate and the titanium dioxide film.

- 98. (withdrawn): The titanium dioxide photocatalyst structure according to claim 97 wherein the precoat film has a thickness of  $0.02~\mu m$  to  $0.2~\mu m$ .
- 99. (withdrawn): The titanium dioxide photocatalyst structure according to claim 97 wherein the precoat film is composed of SiO<sub>2</sub>.
  - 100. (previously presented): A method comprising the steps of:

manufacturing a continuous glass float ribbon having a thickness of 0.125 inches, the glass float ribbon moving at a line speed of 434 inches per minute, and having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath, the float ribbon having silicon and silica coatings deposited on the opposite major surface, the silica coating being deposited at a thickness of about 339Å,

positioning a chemical vapor deposition coating apparatus including a precursor tower and a reactor face over the surface of the float ribbon at a point in the manufacture of the float ribbon where the temperature is 1140°F,

directing a precursor gas mixture containing, by volume percent, 0.5% titanium tetrachloride, 1.9% ethyl acetate and 97.6% helium through said chemical vapor deposition apparatus over a surface of the float ribbon, the precursor gas mixture having a flow rate of 491.6 liters per minute, the temperature of the precursor tower being 400°F and the temperature of the reactor face being 500°F, to produce a titanium oxide coating having a thickness of 684Å, the

titanium dioxide being in the crystalline phase as a photocatalytically-activated, self-cleaning coating over the glass float ribbon, whereby said coating has a photocatalytically-activated self-cleaning reaction rate of 0.029 cm<sup>-1</sup>min<sup>-1</sup>.

101. (previously presented): A method comprising the steps of:

manufacturing a continuous glass float ribbon having a thickness of 0.125 inches at a line speed of 434 inches per minute, the glass float ribbon having a first major surface and an opposite major surface defined as a second major surface, the first major surface having tin diffused therein characteristic of forming the glass float ribbon on a molten tin bath;

depositing a coating over at least one of the major surfaces by positioning a chemical vapor deposition coating apparatus including a precursor tower and reactor face over the surface of the float ribbon at a point in the manufacture of the float ribbon where the glass float ribbon is 1140°F, directing a precursor gas mixture comprising, by volume percent, 0.5% titanium tetrachloride, 1.9% ethyl acetate and 97.6% helium through the chemical vapor deposition coating apparatus over a surface of the float ribbon, the precursor gas mixture having a flow rate of 491.6 liters per minute, the temperature of the precursor tower being 400°F and the temperature of the reactor face being 500°F, to produce a titanium oxide coating having a thickness of 684Å, the titanium dioxide being in the crystalline phase as a photocatalytically-activated, self-cleaning coating over the glass float ribbon, whereby said coating has a photocatalytically-activated self-cleaning reaction rate of 0.029 cm<sup>-1</sup>min<sup>-1</sup>.

102. (previously presented): A method comprising steps of:

providing a continuous glass float ribbon having a thickness of 0.125 inches, the glass float ribbon moving at a line speed of 434 inches per minute, having at least one surface and being manufactured by a float manufacturing process, the glass float ribbon having silicon and silica coatings deposited thereon, the silica coating being deposited in a thickness of about 339Å; and

depositing a photocatalytically-activated, self-cleaning coating of titanium dioxide over the surface of the article at a temperature of 1140°F by chemical vapor deposition using a precursor gas mixture at a flow rate of 491.6 liters per minute and containing, by volume percent, 0.5% titanium tetrachloride, 1.9% ethyl acetate and 97.6% helium during the glass manufacturing process so that the coating has titanium dioxide in the crystalline phase and has a thickness of 684Å, whereby said coating has a photocatalytically-activated self-cleaning reaction rate of 0.029 cm<sup>-1</sup>min<sup>-1</sup>.